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Photocatalytic Oxidation of Ciprofloxacin Under UV-LED Light

Of the Bachelor of Science Degree at
Worcester Polytechnic Institute, Worcester, MA

Submitted by:

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Professors John Bergendahl and Robert Thompson, Faculty advisors

March 10, 2013

Abstract

The objective of this project was to study the degradation and removal of ciprofloxacin (CIP) from water utilizing three phases of titania photocatalysts, anatase, rutile, and anatase/rutile, and two different ultra violet light sources. The light sources included a mercury lamp (254 nm) and light emitting diodes, or LEDs (360 nm). The concentration of CIP remaining after treatment over time was quantified using a UV spectrophotometer. The results showed that both treatment methods were capable of removing high concentrations of CIP from water. Anatase phase titania appeared to be the best performing photocatalyst. Experiments also showed that CIP had an affinity for adsorption to each titania phase. Treatment was performed with low power supply under bench scale batch conditions.

Acknowledgements

This Major Qualifying project could not have been completed without the continual support and guidance from professors Robert Thompson and John Bergendahl. Special recognitions also go out to Professor Michael Timko and Zhenhong Yu for their support as representatives of Aerodyne Research, and Douglas White for assistance with X-ray diffraction operation. All of their contributions helped to ensure the success of this project.

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Chapter 1: Introduction

In recent years, more than 100,000 new chemicals of unknown toxicity and effects to humans and wildlife have been released into our waterways. The European Commission has stated that 99% of these are not adequately regulated and there is no proper safety information for 95% of them. These contaminants include compounds used in everyday life, such as surfactants, pharmaceuticals, paints, and hormones. These chemicals are of particular concern because of the amount of these substances used and because of their activity as endocrine disrupting compounds (EDCs), which have been attributed to cancer, birth defects, hormonal disruptions, and other developmental problems in both humans and wildlife (Hassan, Ginkel, & Oh, 2010).

A number of pharmaceutical and personal care products (PPCPs) have been detected in many natural water systems globally, including rivers, lakes, and reservoirs. The entry of PPCPs into the environment can result in inadvertent exposure of non-target organisms, resulting in a range of potential impacts. For example, widespread use of antimicrobial products and prescription antibiotics has been implicated in the selection for antibiotic-resistance in bacteria (Chee-Sanford, Aminov, Krapac, Garrigues-Jeanjean, & Mackle, 2001). Additionally, environmentally relevant levels of the synthetic estrogen ethinylestradiol found in oral contraceptives have been shown to cause reproductive failure in fish (Nash, Kime, Van der Ven, Wester, Brion, & Maack, 2004). The United States Environmental Protection Agency has heightened government awareness of the possible hazards associated with PPCPs, and has even created a website that lists the published literature relevant to PPCPs as potential environmental contaminants. This website also contains a listing of Drug Disposal and Environmental Stewardship Contamination topics, and now includes over 2000 publications (Gibbons, Wang, & Ma, 2011).

Conventional wastewater treatment processes, such as activated sludge treatment and subsequent clarification, are not very effective at completely removing all PPCPs from wastewater. Therefore, more advanced treatment processes have recently attracted more attention. Activated carbon adsorption, ozonation or advanced oxidation, and membrane separation are all promising advanced treatment processes that are capable of removing many of the PPCPs commonly found in wastewater. Ozone is extremely reactive with some pharmaceuticals, such as estradiol and estrogen due to their functional groups and structures that are readily attacked by ozone (Yang, Flowers, Weinberg, & Singer, 2011). However, little literature exists on the ozonation of pharmaceuticals in

actual pharmaceutical wastewater. Furthermore, details of process optimization and kinetics for the elimination of pharmaceuticals using ozone are limited. Also, there is contradictory information for the ozone dose necessary for pharmaceutical removal. As with all oxidation processes, the degradation products must be analyzed as they may be more toxic than the parent compound. It must also be considered that other compounds in the waste stream other than the target pharmaceutical may produce more harmful by-products as a consequence of the ozonation process. The main disadvantage of ozonation is that in general the target compounds are not fully mineralized, but merely transformed, and so even more harmful substances can be produced as a result. Therefore, an additional treatment such as sand filtration is often required to break down reactive oxidation products. This makes ozonation associated with higher energy costs (Deegan, et al., 2011).

The general difficulty with powdered activated carbon treatment lies in separating the carbon from the water. Various options are available such as sedimentation, which necessitates the use of precipitants, or via membrane filtration, which requires additional energy. The filtration step reduced blocking of the micropores by high molecular weight compounds. Consequently, powdered activated carbon is only suitable for the treatment of pre-treated wastewaters or wastewaters with a low organic loading (Deegan, et al., 2011).

Membrane processes, such as microfiltration and ultra filtration, are generally not fully effective in removing organic contaminants as pore sizes vary from 100-1000 times larger than the micropollutants, which can slip through the membranes. Nanofiltration and Reverse Osmosis have been the focus of attention; however, the studies on the use of these processes for pharmaceutical removal are limited. Though both nanofiltration and reverse osmosis treatment show potential as an efficient method for removing pharmaceuticals from the wastewater, the disposal of the sludge, which could contain the pollutant in a more concentrated form, remains a problem (Deegan, et al., 2011).

The processes mentioned above are all promising techniques, but comparisons among these technologies are problematic since most researchers used synthetic water rather than actual wastewater samples, and because these techniques still require research to improve treatment efficiencies, identify degradation compounds and to determine cost and feasibility of full-scale applications. The oxidation process described in this paper is another proposed option for degradation of pharmaceuticals in wastewater for consideration that could outperform the conventional and advanced processes used currently. It is proposed that water purification using a

new technology of high-power density UV-LED light source with titania nanoparticle photocatalysts provides superior removal of contaminants. The purpose of this project was to determine the degree of removal of pharmaceutical ciprofloxacin (CIP) in water samples to provide data supporting the feasibility of this novel approach to water purification.

Chapter 2: Background

This chapter discusses the past findings related to the occurrence and fate of Ciprofloxacin (CIP) and other pharmaceutically active compounds (PhACs) in the aquatic environment. Studies have shown that PhACs, and more specifically CIPs, are present in various wastewater streams from hospitals and in effluents from municipal waste treatment plants. Much of the concern regarding the presence of PhACs in wastewater and their persistence through wastewater treatment processes is related to the concern that they may contribute to the prevalence of resistance to antibiotics in bacterial species in wastewater effluents and surface waters near wastewater treatment plants (Feroz, Senthikumar, & Rao, 2012). The chemical nature and pharmacokinetics of Ciprofloxacin (CIP) are discussed, as well as the associated environmental and health risks. Furthermore, a discussion of proven removal methods of CIP and other PhACs from water sources is provided.

2.1 Pharmaceuticals in the environment

The occurrence of pharmaceutically active compounds (PhACs) in the aquatic environment has been recognized as one of the emerging issues in environmental chemistry. Although detected at low concentrations, drugs can have adverse effects on aquatic organisms in the environment. Antibiotics, such as ciprofloxacin, are specifically designed to disrupt microbial biochemical processes, and therefore might have a detrimental effect (Brosche, 2010). Several PhACs have been found in sewage influent and effluent samples and in several surface waters located downstream from municipal sewage treatment plants (STPs). Studies show that some PhACs originating from human therapy are not eliminated completely during wastewater treatment in the municipal STPs, and are also not biodegraded in the environment. Positive findings of PhACs have also been reported in groundwater contaminated by landfill leachates or manufacturing residues (Heberer, 2002). The figure below shows a schematic of the possible pathways medicinal products could take to end up in drinking water sources. Removal of these contaminants before reaching this end fate is of increasing concern.

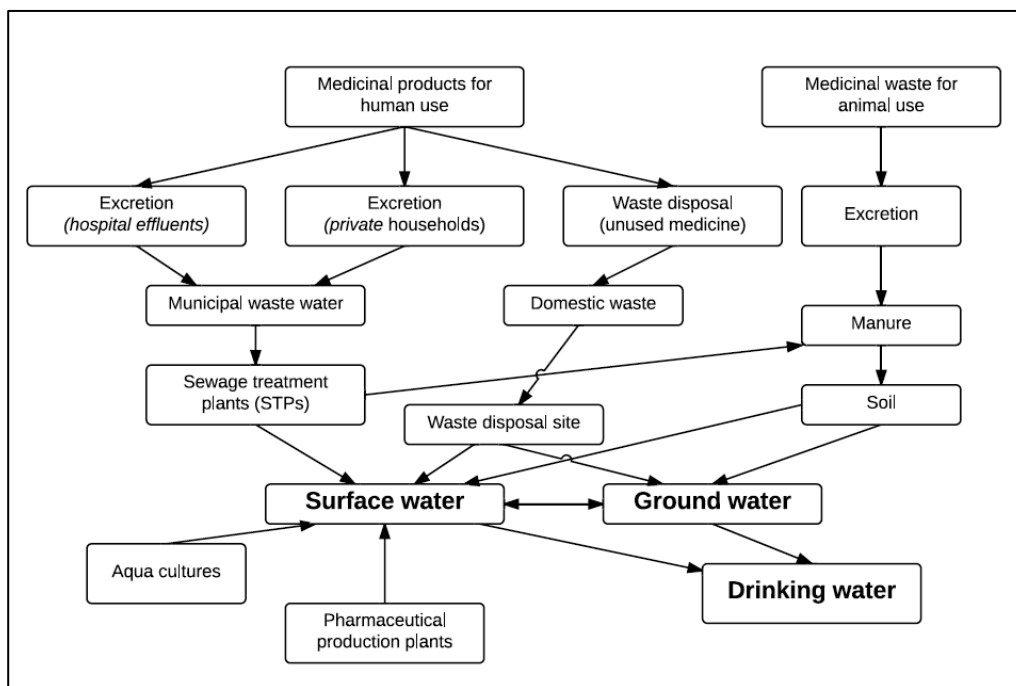


Figure 1 Schematic of possible pathways for the occurrence of pharmaceutical residues in the environment (Heberer, 2002)

There are four general methods for treating pharmaceuticals in wastewater – physical, chemical, thermal and biological. Physical treatment includes filtration and sedimentation to remove particulate contaminants. Chemical treatments take advantage of specific pharmaceutical's chemical properties to neutralize the wastewater. Thermal treatments include incineration and thermal decomposition of waste using controlled heating processes. And biological treatment uses microorganisms to remove biodegradable organic matter and convert organics into food (Bukhari).

The activated-sludge process was developed in 1914 and involves the production of an activated mass of microorganisms capable of stabilizing the organic content of a waste. The biological organisms use the absorbed material as food and convert it to inert insoluble solids and new bacterial cells. The generation of activated sludge is a slow process and the amount so formed from any volume of wastewater during treatment is small and inadequate for the rapid and effective treatment of the wastewater, which requires large concentrations of activated sludge

(Long). Because most PhACs are nonbiodegradable in nature, these compounds are introduced into water streams as contaminants.

In the last decade, the use of membranes in wastewater reclamation has attracted much attention. Membrane bioreactors have a high sludge retention time and are not limited by the settling characteristics of sludge, giving it the upper-advantage over the conventional activated-sludge (CAS) process (Jelena Radjenovic, 2006). However, membrane fouling remains a major drawback, limiting the wider application of this process (UNESCO Centre for Membrane Science and Technology). The occurrence and resilience of these pharmaceuticals have led to further studies into other removal methods that efficiently remove PhACs from the aquatic environment that will be discussed further later in this chapter.

2.2 Ciprofloxacin

Ciprofloxacin (CIP) was introduced in the 1980s as a broad-spectrum fluoroquinolone, a pharmaceutical used in the treatment of a variety of bacterial infections, particularly those caused by Gram-negative pathogens (Davis R, 1996). The fluoroquinolone group is one of the most important pharmaceuticals used worldwide for human and veterinary purposes, thus several studies have reported the environmental presence of these substances, which may pose serious threats to the ecosystem and human health by inducing proliferation of bacterial drug resistance (An, Yang, Li, Song, Cooper, & Nie, 2010).

Ciprofloxacin is considered one of the most useful agents in antibacterial therapy, acting as an inhibitor of DNA-gynase (Ivanov DV, 2006). Figure 2 below shows the chemical structure of CIP.

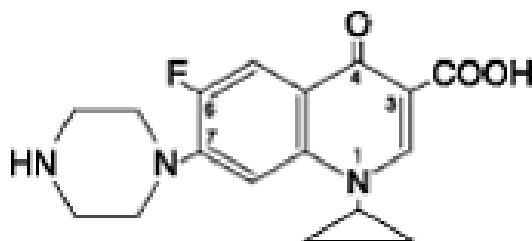


Figure 2: Chemical Structure of Ciprofloxacin (Cipro, 2012)

CIP differs from other quinolones in that it has a fluorine atom at the 6-position, a piperazine moiety at the 7-position and a cyclopropyl ring at the 1-position. The bacterial action of ciprofloxacin results from its interference with the enzyme DNA gyrase, which is needed for the synthesis of bacterial DNA. CIP does not cross-react with other antimicrobial agents such as beta-

lactams or aminoglycosides; therefore, organisms resistant to these drugs may be susceptible to CIP. *In vitro* studies have shown that additive activity often results when CIP is combined synergistically with other antimicrobial agents such as beta-lactams, aminoglycosides, clindamycin, or metronidazole. CIP is indicated for the treatment of infections caused by susceptible strains of microorganisms in the following conditions: acute sinusitis, lower respiratory tract infections, urinary tract infections, acute uncomplicated cystitis in females, chronic bacterial prostatitis, complicated intra-abdominal infections, skin and skin structure infections, bone and joint infections, infectious diarrhea, typhoid fever, uncomplicated cervical and urethral gonorrhea, and inhalational anthrax (post-exposure).

There are several risks associated with CIP, however. It can cause lameness in immature dogs, as well as permanent lesions of the cartilage of weight-bearing joints. In human patients, convulsions, increased intracranial pressure, and toxic psychosis have been reported. Cipro may also cause central nervous system events including: dizziness, confusion, tremors, hallucinations, and depression. Serious and fatal reactions have been reported in patients receiving concurrent administration of CIP and theophylline; these reactions include cardiac arrest, seizure, status epilepticus, and respiratory failure. Although these adverse effects have been reported in patients receiving theophylline alone, the possibility that these reactions may be potentiated by CIP should not be eliminated. Serious and occasionally fatal hypersensitivity reactions have been reported in patients receiving therapy (Bayer, 2000).

Research shows that it is not readily biodegradable in water (Sun, Guo, Sun, Shi, Zhang, & Zhou, 2009). Indeed, ciprofloxacin in water is mainly moved from one phase to another but not really degraded after treatment by traditional WWTP's, and therefore the increased demand of pharmaceuticals has created a rising concern for the potential risks associated with CIP in the environment. Ciprofloxacin's production and use is suggested to result in a release to the environment through various waste streams. In a previous clinical trial, it was shown that 19% of an oral dose of CIP was excreted as metabolites in both urine and feces (LeBel, 1988). In another study, CIP was detected in wastewater streams from hospitals and in municipal waste treatment plants (U.S. National Library of Medicine).

The following section provides further detail into the research evaluating the environmental risks associated with CIP. The goal of this project was to determine feasible methods for the removal of Ciprofloxacin from water to reduce these environmental risks.

2.3 Ciprofloxacin in the environment

2.3.1 Occurrence

Fluoroquinolones, including ciprofloxacin, hold the fourth position in the European market of antibiotics. They have been found in various sewage and surface water samples up to the low $\mu\text{g/l}$ -level. In tests performed in primary and tertiary wastewater effluents in Switzerland, ciprofloxacin occurred at concentrations between 249 and 405 ng/l. Another analysis of hospital effluents detected ciprofloxacin levels between 3 and 87 $\mu\text{g/l}$ (Heberer, 2002).

As demonstrated by these studies, as well as others, CIP is frequently present in the environment, proving that wastewater treatment facilities are inconsistent in their ability to remove CIP. This occurrence is critical to study because there are associated environmental and health risks, which are detailed in the following section.

2.3.2 Environmental and human risks

Being produced and applied with the aim of causing a biological effect, the occurrence in the environment of pharmaceuticals is of ecotoxicological interest. When pharmaceuticals that are not metabolized are excreted by a consumer or flushed down a drain they enter wastewater streams. Pharmaceuticals can enter the environment from other sources as well, such as emission from production sites, direct disposal of surplus drugs in households, therapeutic treatment of livestock in fields, and effluents from fish farms (Zwiener & Frimmel, 2000). Therefore, it is important to consider both point sources as well as diffuse sources as possible routes to the environment. If these contaminants are not sufficiently removed during wastewater treatment they can enter drinking water supplies, and are unknowingly ingested in small amounts by humans. As a specific microbe is chronically exposed to the antibiotic, bacterial DNA can mutate, creating bacteria that is resistant to the antibiotic. These resistant bacteria can cause infections, creating an increasing health issue (S. R. Nagulapally, 2008).

A factor used to describe bacterial vulnerability to antibiotics is minimum inhibitory concentration (MIC). The MIC for resistance is the lowest in-vitro concentration in which an antibiotic completely hinders the growth of bacteria. The MIC for reduced susceptibility is the concentration at which bacteria can survive and indicates the development of intermediate resistance. Organisms that manage to survive between the two MIC points develop intermediate resistance and bacteria that exist at higher concentration have a greater resistance to the antibiotic. A study performed by Nagulapally et al. collected samples of fecal coliforms like *E. Coli* and

enterococci from influent and effluent waters. Intermediate and high resistance was observed for CIP (S. R. Nagulapally, 2008).

Halling – Sorensen et al. studied the effects of CIP and two other antibiotics on an aquatic environment. They investigated the toxicity of the three antibiotics towards sludge bacteria, green alga, cyanobacterium, a crustacean, and a fish. CIP was highly toxic to the cyanobacterium. After performing a risk characterization, it was predicted that of the three antibiotics, CIP had the greater risk (B. Halling - Sørensen, 2000).

In another study, CIP was found in concentrations between 0.7 and 124.5 µg/l in effluents from hospitals and was assumed to be the main source of genotoxic effects measured with the umuC test in hospital effluents. Kummerer, Al-Ahmad and Mersch-Sundermann found through HPLC analysis that their toxicity controls did experience an inhibitory effect within the first days on bacteria able to degrade sodium acetate because there was no elimination of ciprofloxacin in the tests. After an adaptation period the inoculum biodegraded readily biodegradable sodium acetate well in the presence of the quinolones. This allowed them to conclude that the antibiotics that they tested were not biodegraded in the CBT, and consequently their genotoxicity was not eliminated (Kummerer, Al-Ahmad, & Mersch-Sundermann, 2000).

Nagulapally et al. evaluated the occurrence of antibiotic-resistant bacteria in aqueous samples obtained from a municipal wastewater treatment plant. Samples from the influent, clarifier effluent, and disinfected effluent were assayed for fecal coliforms, *E. coli*, and enterococci exhibiting resistance to ciprofloxacin and other antibiotics. The numbers of drug-resistant organisms in influent ranged from nondetectable to 7×10^5 colony-forming units (CFU)/100 mL for fecal coliforms, nondetectable to 5×10^4 CFU/100 mL for *E. coli*, and nondetectable to 6×10^5 CFU/100 mL for enterococci. Intermediate and high resistance was observed for CIP. Figure 2 illustrates the survival of the three bacteria in influent wastewater samples when exposed to various concentrations of CIP.

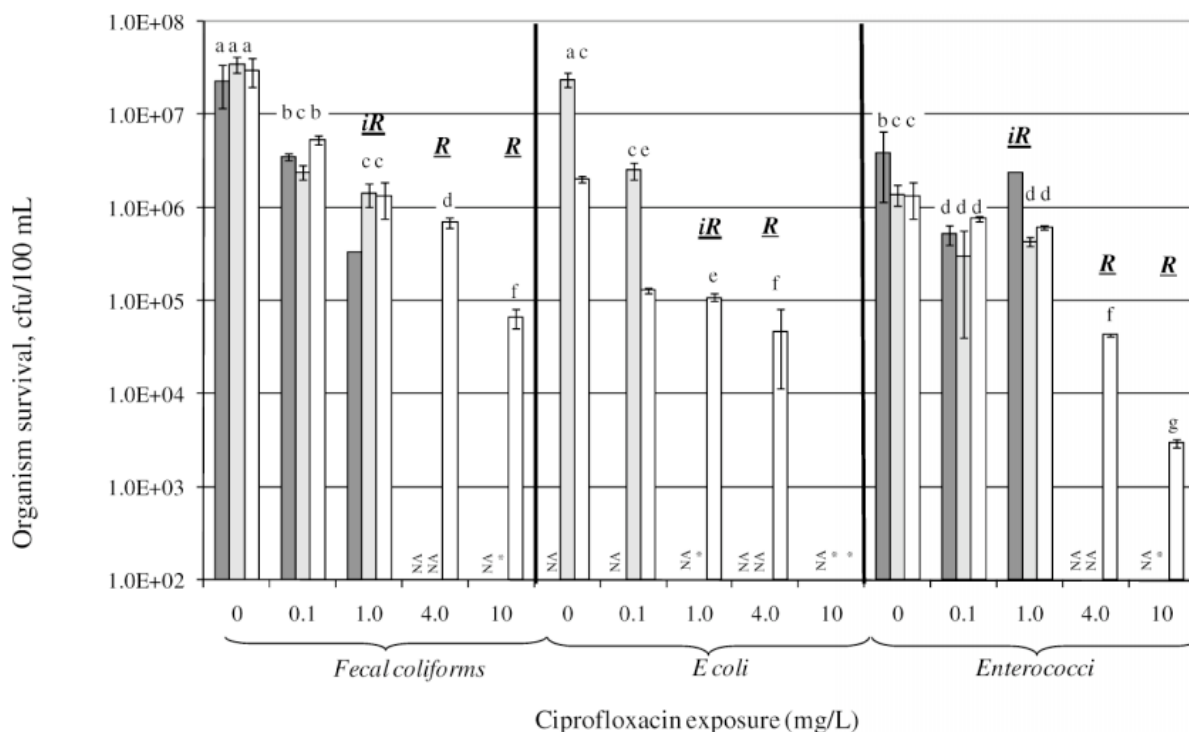


Figure 3 CIP exposure to three bacteria in wastewater samples. Dark grey bars represent summer-time, gray bars represents winter, and white bars represents spring (Nagulapally, Ahmad, Henry, Marchin, Zurek, & Bhandari, 2009)

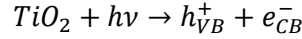
The different shaded bars represent data collected in summer (darkest shade), winter (lighter shade), and spring (white). The number of fecal coliforms and enterococci in the influent wastewater were statistically similar in all seasons, while those for *E. coli* were not. Significant intermediate resistance for CIP (shown by the notation *iR*) was observed in fecal coliforms. 52% of the enterococci showed intermediate resistance to CIP, and complete inactivation of *E. coli* was observed at 1.0 mg/L CIP in winter samples (Nagulapally, Ahmad, Henry, Marchin, Zurek, & Bhandari, 2009). This study shows that antibiotic-resistant bacteria are present in significant numbers in municipal wastewater, which further strengthens the assertion that infections caused by antibiotic-resistant bacteria is hazardous to the environment.

With an increasing number of studies revealing the effects of CIP in water, the argument for removing it becomes stronger. The harmful effects both to the environment and humans described above provide pertinent evidence for its removal.

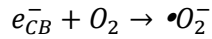
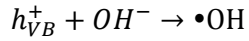
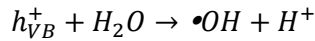
2.4 Titanium Dioxide Photocatalyst

Titanium dioxide (TiO₂), or titania, is a commonly occurring oxide that has a wide range of applications especially as a photocatalyst. In the presence of light, the photons have a higher energy

than the semiconductor band gap, resulting in photons being absorbed, and an electron is promoted to the conduction band, leaving a hole in the valence band. This excited electron is then used directly to drive the chemical reaction.



The degradation performance of TiO_2 is attributed to highly oxidizing hydroxyl radicals. Virtually any organic compound can be completely mineralized with irradiated TiO_2 , except of cyanuric acid, which is fortunately non-toxic (Carp, Huisman, & Reller, 2004).



The electron/hole pair participates in reactions with absorbed molecules on the titania surface within milliseconds. Titania comes in three mineral forms: anatase, rutile, and brookite (Primo, Corma, & Garcia, 2010). In many cases, anatase and rutile forms are used together. For the purposes of this project, the anatase and rutile phases will be described in the following subsection.

2.4.1 Anatase vs. Rutile Titania

Anatase is found as small, isolated and sharply developed crystals. There is limited information about this form of titania because it is difficult to synthesize single crystals and ceramics of this form. In a study performed by Matsumura et al. it was determined that anatase particles have low activity for the oxidation of water, even when using large particles. However, for oxidation of reactive compounds, such as alcohols, it is known that fine anatase particles are very active photocatalysts, especially when the concentration of the reactants is low (Ohno, Sarukawa, & Matsumura, 2002).

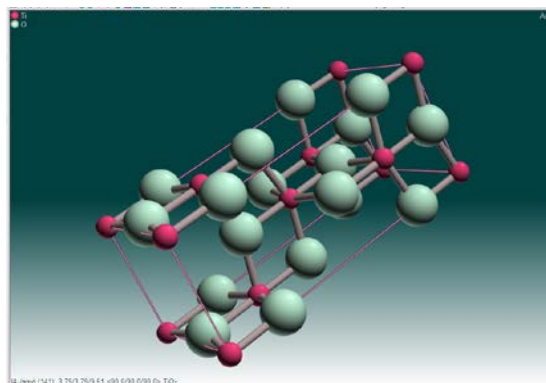


Figure 4 3D crystalline structure of anatase titania (Materials Data Inc, 2011)

Conversely, another study suggests that anatase is recognized as the photoactive phase, while rutile is commonly known as a low-active photocatalyst. In studies performed with rutile and anatase samples of different industrial origin, anatase showed higher catalytic activity towards the photodegradation of cyanide compounds. In another investigation on the water/phenol catalytic oxidation it was found that both phases were active, but anatase had a higher activity. It was also discovered that a sample containing anatase and rutile was more active than a sample of solely rutile phase. Furthermore, one group found no significant differences between the pure forms of the different phases towards the gas-phase photocatalytic oxidation of organic compounds. Therefore, it can be concluded from literature that there is great debate over the elucidation of the crystalline phase responsible for the titania photocatalytic activity towards degradation of organic compounds (Collins-Martinez, Ortiz, & Elguezabal, 2007).

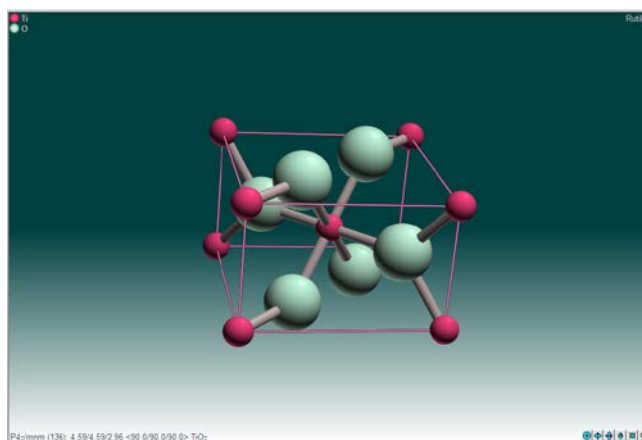


Figure 5 3D crystalline structure of rutile titania (Materials Data Inc, 2011)

2.4.2 Mixed-Phase Titania

There is another known mixed-phase of titania nanoparticles which consists of anatase and rutile, and it is the interface between these two phases which is why it is suggested that this mixed-phase, which will be referred to as anatase/rutile throughout this report, is the more photoactive of the three phases. At the solid-solid interface in nanocomposite materials there is a third, tetrahedral intermediate phase that is created when particles are arranged in a certain way, which is more photocatalytically active than the octahedral formations of the two pure phases. This structure facilitates functions such as charge transfer, trapping, and reaction (Li, Dimitrijevic, Nichols, Rajh, & Gray, 2008). In a study performed by Gray and coworkers, a significantly greater amount of 2,4,5-trichlorophenol (TCP) absorbed at the anatase/rutile phase surface than that of either pure anatase or pure rutile. They proposed that the difference between the surface reactions on anatase/rutile and those on pure-phase TiO_2 was related to the morphology of anatase/rutile, wherein anatase-rutile interfaces gave rise to unique active sites (Li & Gray, 2007).

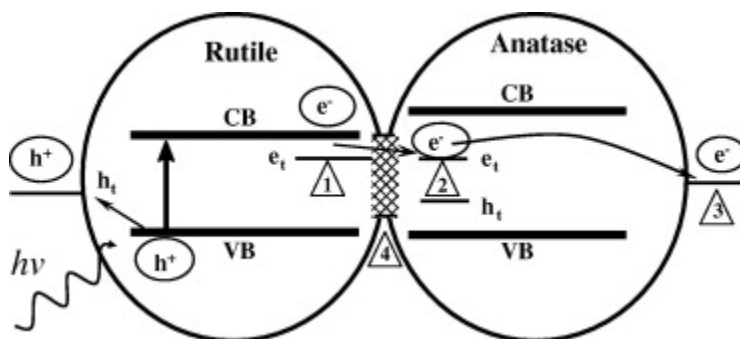


Figure 6 Model of the solid-solid interface in mixed-phase TiO_2 photocatalysts (Li & Gray, 2007)

2.5 Treatment Methods

Most pharmaceutical substances are biologically active and hydrophilic so that the body can consume them easily, and persistent to avoid degradation before they have a medicinal effect. Whether these pharmaceuticals are amenable to treatment will depend on the physicochemical properties of the compound and the key underlying removal mechanisms of the treatment process (Snyder, et al.). Most common processes are activated carbon adsorption, physical separation, and chemical oxidation. Most recently, advanced oxidation processes (AOPs) have emerged as the most investigated treatment method.

2.5.1 Advanced Oxidation

Among the many processes that can degrade contaminants, advanced oxidation processes (AOPs) are a particularly attractive option. These processes rely on the production of reactive

hydroxyl radicals that are able to oxidize almost all organic compounds. (Photocatalytic oxidation of cipro under simulated sunlight). AOPs are characterized by their nonselective attack. The versatility of AOPs is also enhanced by the fact that there are different ways of producing hydroxyl radicals, facilitating compliance with the specific treatment requirements. Methods based on UV, $\text{H}_2\text{O}_2/\text{UV}$, O_3/UV , and $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$ combinations use the photolysis of H_2O_2 and ozone to produce the hydroxyl radicals.

Some of the disadvantages associated with AOPs are their high operating costs, which, depending on the specific process, could be due to (i) high electricity demand, as for ozone and UV-based AOPs, (ii) relatively large amounts of oxidants and/or catalysts consumed, as for ozone, hydrogen peroxide, and iron-based AOPs, and slow kinetics, as for photocatalysis with titanium oxide, and (iii) the pH required, as for Fenton and photo-Fenton processes. Due to the relevance of UV use for this project, the following sections will focus on the different applications of UV light to degrade ciprofloxacin in wastewater.

2.5.2 Photolysis

Photolysis involves the interaction of artificial or natural light with the target molecule and the induction of photochemical reactions, which can lead to its degradation to intermediate products whose further decomposition eventually yields mineralized end-products. Ultraviolet treatment has traditionally been employed for the disinfection of drinking water with the advantage of minimizing the formation of any regulated disinfection by-products, as compared to chlorination.

The efficiency of direct photolysis is usually enhanced when irradiation is combined with hydrogen peroxide. Hydrogen peroxide is a strong oxidant whose photolytic dissociation yields hydroxyl radicals to facilitate the process. The efficiency of photolytic degradation depends on several factors such as the absorbance spectrum of the pharmaceutical, the quantum yield of photolysis, the concentration of hydrogen peroxide employed and the water matrix. The presence of natural organic matter acts as a precursor of reactive species and leads to faster degradation due to the production of photochemically induced reactive species (Klavarioti, Mantzavinos, & Kassinos, 2009).

2.5.3 Ozonation

Ozone is a strong oxidant that either decomposes in water to form hydroxyl radicals, which are stronger oxidizing agents than ozone itself, thus inducing the indirect oxidation of certain

functional groups of organic molecules through an electrophilic mechanism. Depending on the substrate and operating conditions, ozone is usually favored at increased pH values due to the increased production of hydroxyl radicals. Furthermore, treatment performance is enhanced if ozone is combined with light irradiation, hydrogen peroxide, or with iron or copper complexes that act as catalysts.

2.5.4 Fenton oxidation

Homogeneous oxidation with Fenton's reagents occurs in the presence of ferrous or ferric ions with hydrogen peroxide via a free radical chain reaction, which produces hydroxyl radicals. It is considered to be a metal-catalyzed oxidation reaction. Process efficiency is closely related to the solution pH whose optimal values are between 2 and 4 as well as the COD-hydrogen peroxide-catalyst ratio in the feed. Efficiency may also be enhanced in the presence of UV irradiation as more hydroxyl radicals are produced in the photo-Fenton reaction compared to dark Fenton. Optimization of the catalyst and oxidant concentrations relative to the effluent's polluting load renders the process suitable to treat strongly polluted effluents from hospitals and pharmaceutical manufacturing. In most cases, Fenton's oxidation is capable of mineralizing a substantial amount of polluting load, yielding effluents that are less toxic and more readily amenable to biological post-treatment.

Fenton systems are easy to handle and operate. By adjusting working conditions accordingly, Fenton's reactions may conveniently be employed to treat micro-pollution caused by residual pharmaceuticals in industrial effluents as well as surface waters with increased organic loading. Use of ferrous or ferric salts usually suffers two major drawbacks associated with (a) the narrow pH range of operation to avoid the formation and subsequent precipitation of iron oxyhydroxides and (b) the need to recover dissolved ions from the treated solution, thus requiring an additional treatment stage. Immobilization of Fenton's catalyst on a heterogeneous matrix would enable its use under non-controlled pH conditions as well as its easy recovery from the treated effluent.

An example of Fenton's oxidation to improve the biodegradability of a pharmaceutical in water is shown by Tekin et al. They performed treatability studies, such as an analysis of chemical oxygen demand (COD) and a 5-day biochemical oxygen demand (BOD₅). They found that higher hydrogen peroxide doses generated more hydroxyl radicals, which improved the COD removal efficiency. 2.5M hydrogen peroxide yielded COD removals higher than 50%, and by keeping this dosage constant and varying the Fe²⁺ dosage they determined that increasing the Fe²⁺ dosage from

0.003 M to 0.01 M doubled the average COD removal efficiency. Increasing the dosage any further lowered the COD removal efficiency. This, they hypothesized, could be due to the scavenging action of superfluous Fe^{2+} for the hydroxyl radical.

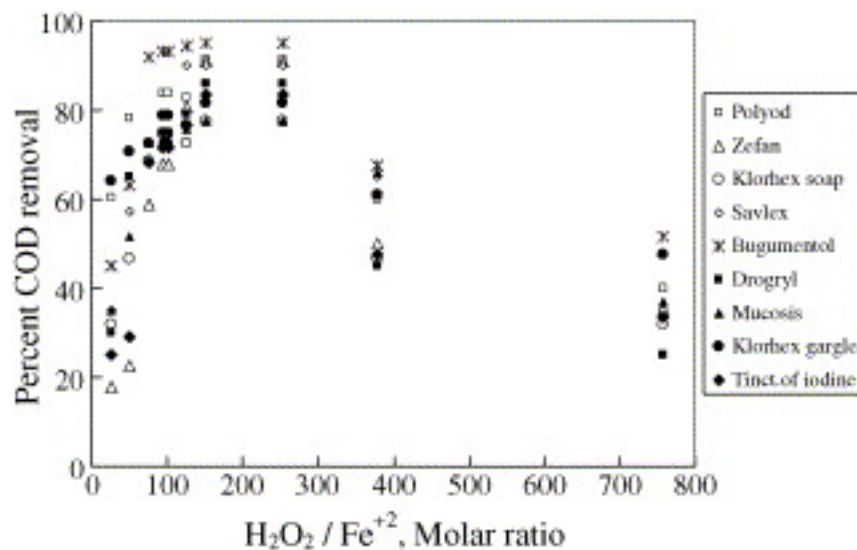


Figure 7 Relationship between COD removal efficiency and $\text{H}_2\text{O}_2/\text{Fe}^{+2}$ dosage (Tekin, et al., 2006)

This indicated that the efficiency of treatment is dependent on the amounts of H_2O_2 and Fe^{2+} available in the system. When either is overdosed, both substances can react with the hydroxyl radicals and inhibit the oxidation reactions. However, several other sources reported different ratios when dealing with different types of waste. Overall, treatment with Fenton's oxidation improved the biodegradability and reduced the toxicity of the pharmaceutical wastewaters (Tekin, et al., 2006).

2.5.5 Portable Water Purification Techniques

Water purification is not only important to reduce the contaminants in pharmaceutical and industrial plant effluent streams, but it is also necessary to have self-contained units, or efficient point-of-use (POU) water treatment system, for campers, survivalists, military personnel, and others who must quickly obtain drinking water from untreated sources such as rivers, lakes, etc. in remote or rural areas or storm-ravaged communities. Boiling kills pathogens and can drive out some of the volatile organic compounds present in water, but is not routinely used except in emergencies. It should never be used when toxic metals, chemicals or nitrates are in the contaminated water, and can concentrate harmful contaminants that do not vaporize. Distillation consistently produces very pure water, but is costly, requires electricity and routine cleaning, and is

timely. It can take two to five hours to make a gallon of pure water (Review of Drinking Water Treatment Methods).

Reverse osmosis (RO) significantly reduces salt, most inorganic material, and some organic compounds in water. However, RO systems waste about two to four gallons of wastewater for each gallon of filtered water produced. Additionally, some pesticides, solvents, and other volatile organic compounds are not completely removed by RO, and damaged membranes are not easily detected. Filters remove suspended sediment and small organic particles, but will not remove contaminants that are dissolved in water. Activated carbon is most commonly implemented for pre-filtering or post-filtering as a secondary means to complement another purification technique. They will become less effective over time, and there is often no noticeable indication of this occurring. In solar water disinfection, water is oxygenated by shaking partially filled capped plastic PET bottles, filled, and placed in full sun for six hours, or in partial sun for two days, to raise the temperature of the water for extended UVA radiation to kill microbes. Ultra Violet (UV) light is advantageous because it requires very little contact time, and destroys organic contaminants and microorganisms, while keeping minerals intact. However, it is not suitable for water with high levels of suspended solids, turbidity, or color because these materials can react with UV radiation, and reduce performance (Review of Drinking Water Treatment Methods). Therefore a powerful, time efficient, and economically feasible purification device is still needed for situations requiring more immediate portable drinking water.

2.6 Advanced Oxidation with UV light with Hydrogen Peroxide

A Major Qualifying Project completed in 2011 at Worcester Polytechnic Institute studied the removal of ciprofloxacin from water using UV light combined with hydrogen peroxide (H_2O_2) (Roma, Weller, & Wentzell, 2011). This treatment method was compared to two other treatment methods, UV photolysis and adsorption of two types of granular activated carbons, and found that the addition of hydrogen peroxide to UV treatment doubled the rate of CIP removal that occurred using UV photolysis by itself. However, it degraded approximately the same percentage of CIP once equilibrium was reached.

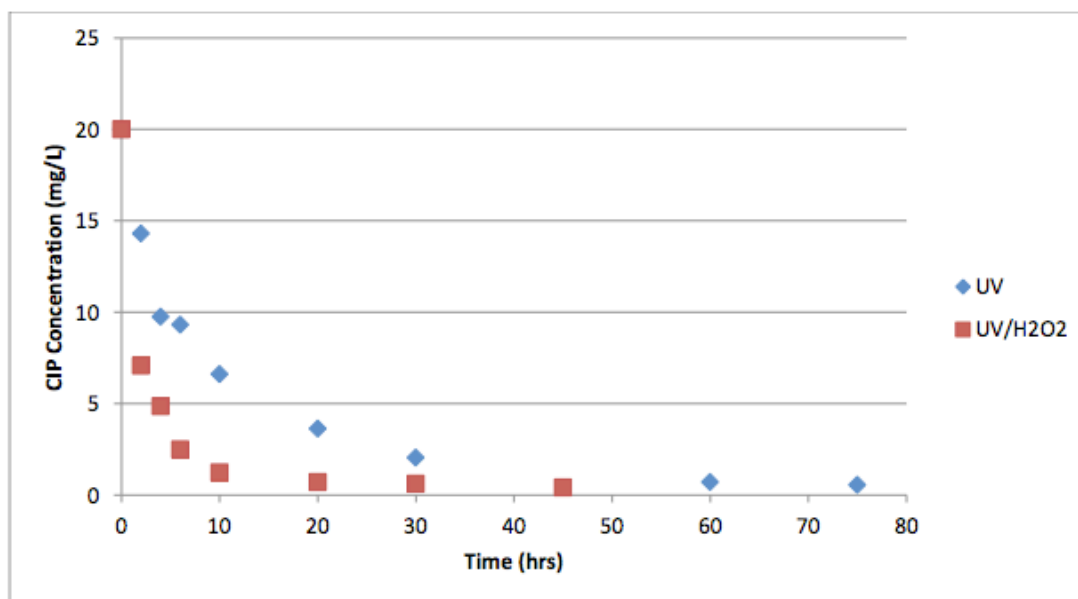


Figure 8 Comparison of rate of removal of CIP using UV and UV/ H_2O_2 (Rosario-Ortiz, Wert, & Snyder, 2010)

Another group similarly evaluated the performance of advanced oxidation treatment using low pressure UV light coupled with hydrogen peroxide for the oxidation of six pharmaceuticals in three wastewater effluents. The removal ranged between no observed removal and greater than 90% removal. Their results indicated that the efficacy of UV/ H_2O_2 treatment of the removal of pharmaceuticals from wastewater was a function of not only the concentration of effluent organic matter but also its inherent reactivity towards hydroxyl radicals. They also showed that the removal of pharmaceuticals also correlated with reductions in UV absorbance at 254 nm, which offers a surrogate to assess pharmaceutical removal efficacy during UV/ H_2O_2 treatment (Rosario-Ortiz, Wert, & Snyder, 2010).

2.7 Light Sources for Photo-oxidation

The TiO₂-catalyzed photocatalytic oxidation process typically requires a light source with a wavelength below 388 nm. Mercury vapor lamps have been widely used in laboratory and commercial photocatalytic systems. However, these lamps are fragile and have a relatively short life span. Mercury is a highly toxic and controlled substance being banned by government safety and environmental regulators. Although there are nonmercury lamps available, such as microwave UV sources, they are driven by magnetrons that must withstand long duty cycles and the microwaves must be contained for safety purposes (Levine, Richards, Coutts, Soler, & Maxik, 2011).

Light-emitting diodes (LEDs) are compact, reliable and long-lasting devices. LEDs are driven by direct current, can accommodate rapid “on” and “off” toggling, and do not contain toxic mercury. The light output from a single device has increased by a factor of 20 per decade while the price in US dollars per lumen has declined by a factor of 10 per decade, since the development of the first commercial LEDs in 1968 (Steele, 2007). White-light LEDs are now surpassing the efficiency of linear fluorescent and compact fluorescent lamps. Ultra-violet-light-emitting diodes (UV-LEDs) have a life expectancy of 50,000 hours, about five times that of mercury vapor lamps. Naturally, they are being considered as an alternative UV source for photocatalysis; however, little data is available to address the central question whether UV-LEDs could serve as an effective photon source in heterogeneous photocatalytic oxidation (Levine, Richards, Coutts, Soler, & Maxik, 2011).

2.8 Summary

The occurrence of CIP in aquatic environments is a cause for concern because of the possibility that bacteria can become resistance to the antibiotic and thus causes infection. While the performance of several treatment methods have been studied in the past, not much is currently known about the performance of titania photocatalyst and UV-LED light. This project will provide knowledge on the new treatment method that has the potential to compete with the methods mentioned above, as well as others, that have been used in the past.

Chapter 3: Methodology

3.1 Sample Preparation

Solutions containing known initial concentrations of CIP were created using CIP obtained from LKT Laboratories and purified water (ROpure ST Reverse Osmosis/tank system).

Predetermined masses of CIP were weighed out using a Mettler Toledo (AB104-S) scale (± 0.01 mg) and mixed with purified water. To ensure that the CIP was thoroughly dissolved in solution, a magnetic stirrer was applied for 20 minutes. Sodium hydroxide (0.1 M) and hydrochloric acid (0.1 M) were used to maintain all solutions at pH7.

For samples used in photocatalytic degradation studies, the photocatalysts in anatase (99.9+% pure, 10-25 nm), rutile (99.9+% pure, 30 nm) and anatase/rutile (99.9+% pure, 20 nm) phase were supplied by Aerodyne Research, Inc., Billerica, MA. Predetermined masses of TiO_2 were weighed out using a Mettler Toledo (AB104-S) scale (± 0.01 mg) and mixed with purified water for control testing or CIP solution. All chemicals were used as received without any further purification.

3.2 Measuring Sample Absorbance

Analysis of samples of CIP solutions was performed before and after treatment to determine the degree of CIP removal for each trial. Studies were executed using a Varian-Cary 50 Scan UV-visible spectrophotometer operating at 270 nm and Varian 10 mm stoppered quartz UV-cells UV-cuvettes (3.5 mL) to measure absorbance.

3.3 X-Ray Diffraction Analysis

The physical characteristics of the TiO_2 photocatalysts were analyzed using the X-ray diffractometer in Goddard Hall (Rigaku Geigerflex, Normal Focus). In many cases, the size of TiO_2 particles is an important factor affecting the performance of the materials. There are several methods of preparation of these particles, such as homogeneous precipitation, hydrothermal methods, and flame synthesis, and each method produces a different powder size. Consequently, phase and particle size are important parameters that may influence the physical properties of the material. Therefore, data on particle size obtained by X-ray diffraction technique was obtained, as size is related to the diffraction peak broadening. XRD methods were also used to identify crystalline phases (Thamaphat, Limsuwan, & Ngotawornchai, 2008).

Samples of the powders were mounted onto glass microscope slides and inserted into the X-ray diffractometer, and a Quick Scan (Materials Data Jade 8) was performed from 5–80 2-theta to obtain a pattern that was matched with patterns in the software database.

3.4 CIP Concentration Standard Curves with Detection Limit

A standard concentration curve was generated using samples of known concentrations at pH7 in order to determine unknown concentrations of treated samples. Solutions of ten known concentrations ranging from 20 mg/L to 0.04 mg/L CIP in water were analyzed with a Varian-Cary 50 Scan UV-visible spectrophotometer to measure absorbance at 270 nm. The absorbance measurements were correlated to the known concentrations and plotted to generate a CIP concentration standard curve. This allowed any concentration within this range to be determined for the trials using treated samples. The limit of detection was also identified by using the STEYX formula in Microsoft Excel to find the standard error in the prediction of absorbance for each concentration and then divided by the slope of the standard curve, then multiplied by a factor of 3.3. This value was the concentration at which there is no longer a statistical difference between pure water and CIP samples. The data table for this analysis can be viewed in Appendix A.

3.5 Reactivity Assessment

To determine if CIP and TiO₂ reacted without the presence of a light source reactivity tests were performed. Three sample solutions of 20-mg/L solution of CIP in purified water were removed from light exposure by sealing beakers in aluminum foil. Each titania phase was placed in one of the three beakers and agitated gently for 36 hours using magnetic stirrers. Periodically, samples of the solution were extracted and filtered using a Micro-mate interchangeable hypodermic syringe equipped with filters (Acrodisc, 0.2 µm), and then analyzed in the spectrophotometer at 270 nm to determine the final absorbance. The absorbance was converted to a final concentration reading using the standard curve to ensure that CIP did not react with the titania without a light source in solution. The results of this assessment can be viewed in Appendix B.

3.6 Ultraviolet Treatment

Ultraviolet (UV) treatment was performed using a UVP Pen-Ray mercury UV lamp (254nm) in batch mode powered by a Spectroline power supply (115V, 60Hz, 0.15Amp). A glass tube apparatus held a UV probe surrounded by approximately 4 mL of solution hooked up to a power source. The reactor was fixed in a volumetric flask (500 mL) enclosed in tin foil to prevent a significant amount of light from escaping from the lamp. Figure 6 displays the reactor set-up.

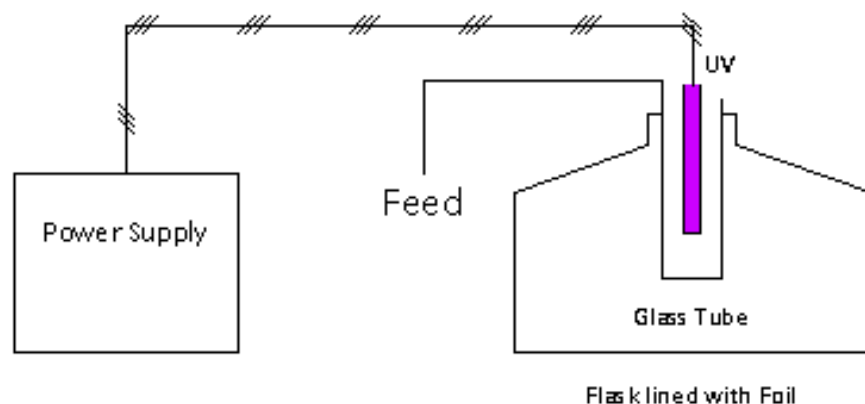


Figure 9 UV (254 nm) Reactor Set Up

Experiments were run at time intervals to closely monitor the effect of time on the treatment. Time trials were conducted with solutions of an initial concentration of 20 mg/L CIP in water.

3.6.1 UV Photolysis on CIP Solution

To verify that CIP does not degrade with only UV light treatment, time trials were conducted on solutions containing only CIP. Treatment was performed at UV light exposure time intervals of 5, 10, 20, 30, 40, 50, and 60 minutes. After each experimental run, the pH of each sample was adjusted to 7 and analyzed by the spectrophotometer to determine the final absorbance. The standard curve was referenced to convert the absorbance into a final concentration.

3.6.2 UV Treatment with Addition of Titania Nanoparticles

Further UV treatment was conducted with the addition of TiO_2 nanoparticles at a concentration of 1000 mg/L. A previous study of the photocatalytic oxidation of ciprofloxacin under simulated sunlight performed by Gad-Allah, Ali and Badawy determined that the optimum concentration of TiO_2 is 1000 mg/L when they ran their tests with 50 mg/L CIP at a solution pH 5.8 and a commercial visible metal halide lamp (HQI-T 250/Daylight) (Gad-Allah, Ali, & Badawy, 2010). The first set of experiments was performed by adding anatase TiO_2 to the solution before implementing the same treatment procedure described above. The second set of experiments used rutile TiO_2 in solution instead of anatase TiO_2 , and the final set of experiments used anatase/rutile TiO_2 in solution. Time trials were performed at intervals of 5, 10, 20, 30, 40, 50 and 60 minutes. After each experimental run was completed, the samples were extracted and TiO_2 was separated

using a syringe and filter apparatus. The resulting solution was analyzed by the spectrophotometer to determine the final absorbance to be related to a final concentration using the standard curve.

3.7 Ultraviolet-LED Treatment

Ultraviolet-LED treatment was performed using UV light emitting diodes (Nichia NC4U133A, 360nm) provided by Aerodyne Research in a lab-scale batch reactor powered by an adjustable power supply also provided by Aerodyne that was fixed to 14 Volts and 1.0 Amps. Figure 7 displays the reactor set-up. Experiments were run at time intervals to closely monitor the effect of time on the treatment. Time trials were conducted with solutions of an initial concentration of 20 mg/L CIP in water.

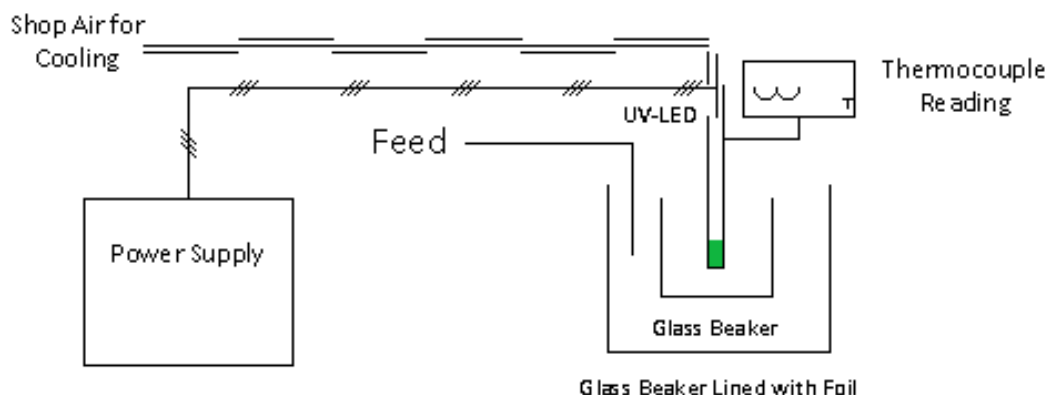


Figure 10 UV-LED (360 nm) Reactor Set-Up

UV treatment was conducted with the addition of TiO_2 nanoparticles at a concentration of at first 1000 mg/L. The first set of experiments was performed by adding anatase TiO_2 to the solution before implementing the same treatment procedure described above. The reaction rate at this titania concentration occurred too rapidly to obtain sufficient data, so the experiment was repeated with 500 mg/L of titania. This concentration was used for the remaining two titania phases. The second set of experiments used rutile TiO_2 in solution, and the final set of experiments used anatase/rutile TiO_2 . Time trials were performed at intervals of 5, 10, 20, 30, 40, 50 and 60 minutes. After each experimental run was completed, the samples were extracted and TiO_2 was separated using a syringe and filter apparatus. The resulting solution was analyzed by the spectrophotometer to determine the final absorbance to be related to a final concentration using the standard curve.

Chapter 4: Results and Discussion

4.1 Standard Curve

A standard curve was plotted at pH 7 using the UV spectrometer at wavelength 270 nm to use as a method of detection after treatment. Figure 8 shows the calibration curve generated from measuring the absorbance at various known concentrations of CIP.

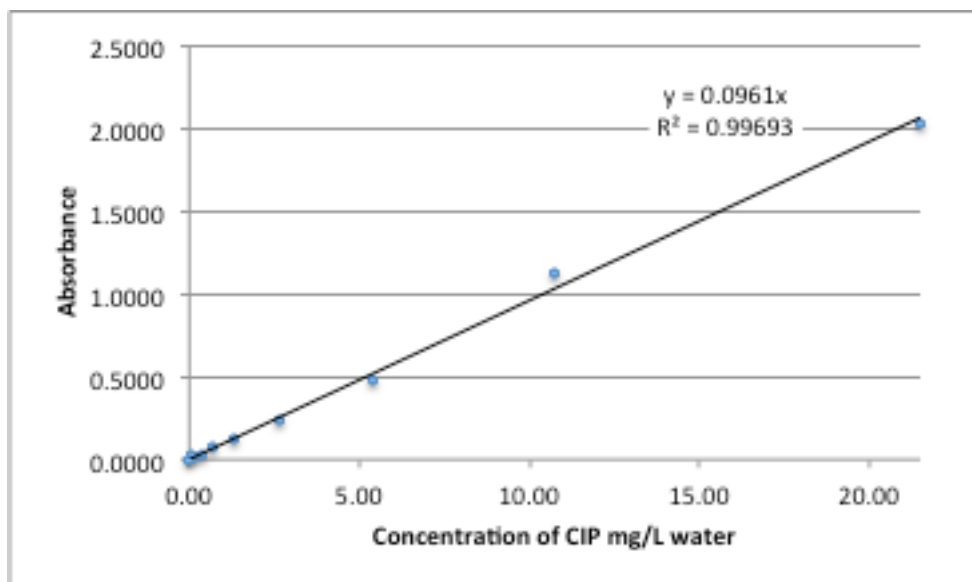


Figure 11 Standard curve to evaluate the concentration of CIP from the absorbance

This curve was considered an accurate form of detection below concentrations of 21.5 mg/L, with a R^2 value of 0.99693, and could therefore be used to detect the concentration of CIP in solution for this project.

4.2 X-Ray Diffraction Analysis

X-ray diffraction was performed on each powdered sample of TiO_2 in order to study the physical properties of the compounds. The patterns for anatase and rutile phases are shown in Figures 12 and 13 respectively.

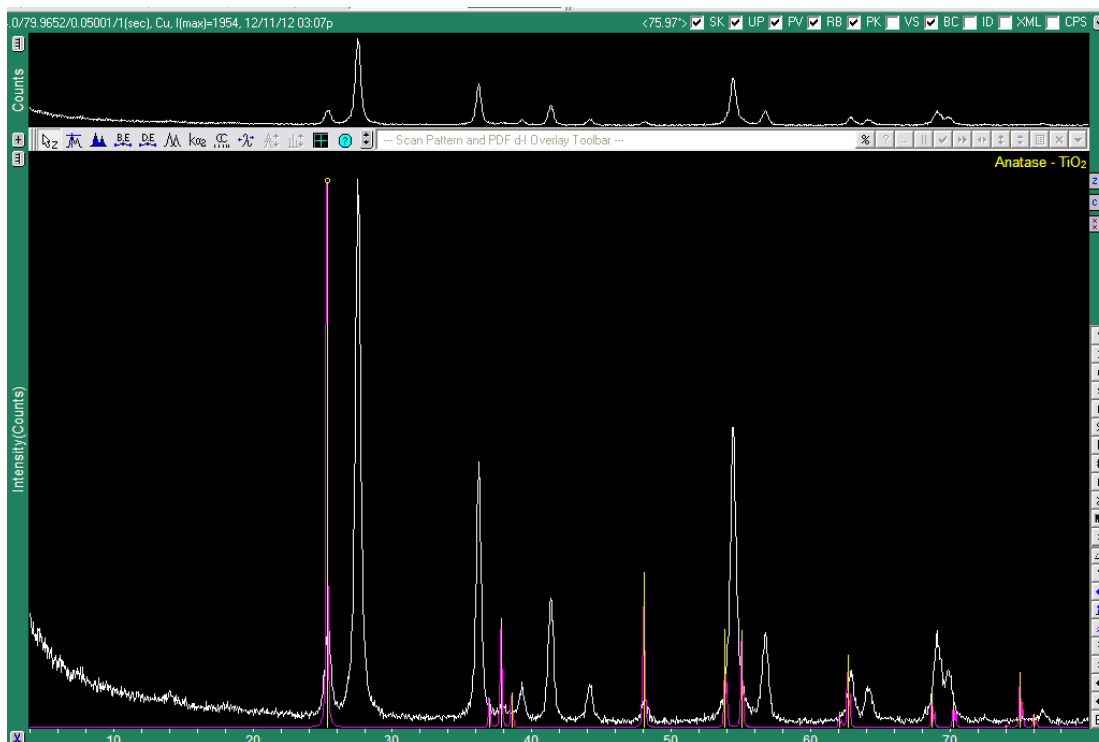


Figure 12 XRD Image of Anatase Phase Titania with database Anatase pattern overlay

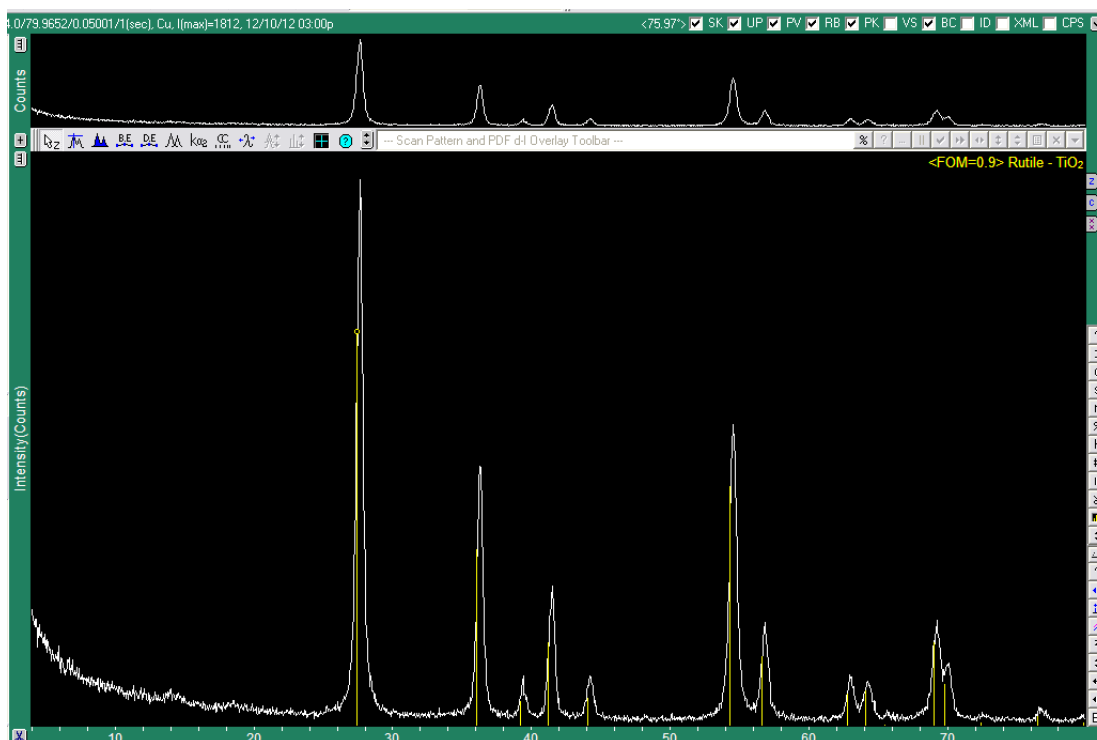


Figure 13 XRD Image of Rutile Phase Titania with database Rutile pattern overlay

XRD analysis done in a past study performed on rutile and anatase phases defined characteristics of the two phases. XRD patterns for rutile phase TiO_2 exhibited strong diffraction peaks at 27° , 36° and 55° 2-Theta, which is apparent in Figure 13. On the other hand patterns exhibited strong diffraction peaks at 25° and 48° 2-Theta indicating anatase phase. It was also determined that diffraction pattern peak intensity increases with increasing particle size, and that nano- TiO_2 powder is composed of irregular polycrystalline domains. Amorphous material was revealed by a broad pattern with low intensity; however the broadening of the XRD pattern of nanosized TiO_2 was concluded to be negligible (Thamaphat, Limsuwan, & Ngotawornchai, 2008). The rutile phase sample matched almost identically with the rutile pattern from the database. However, the anatase sample was not similar to the anatase pattern on file. This indicates that the anatase samples are not structurally similar to the anatase compound in literature, and could have consequently resulted in unexpected adsorption and reactivity behavior.

Since Jade 8 does not have a pattern on file for anatase/rutile, this sample was analyzed with anatase, rutile, and brookite patterns. These patterns are shown in Figures 14, 15 and 16 respectively.

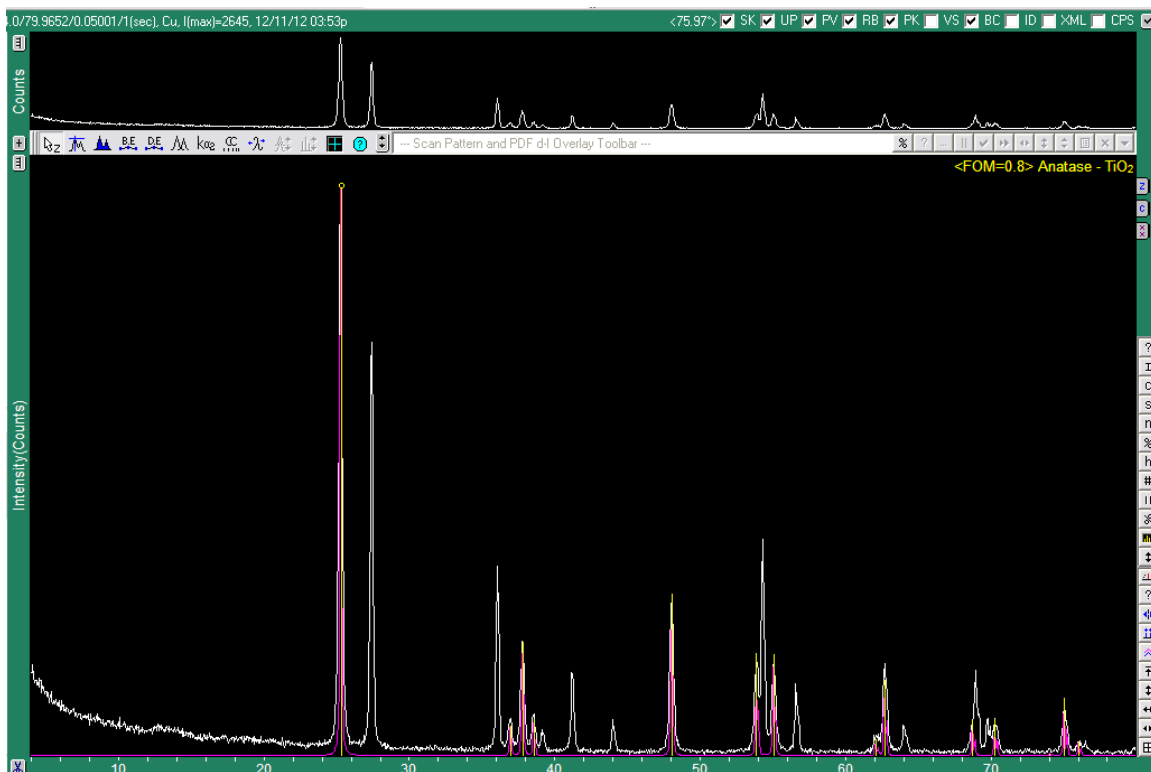


Figure 14 XRD Image of Anatase/Rutile Phase Titania with database Anatase pattern overlay

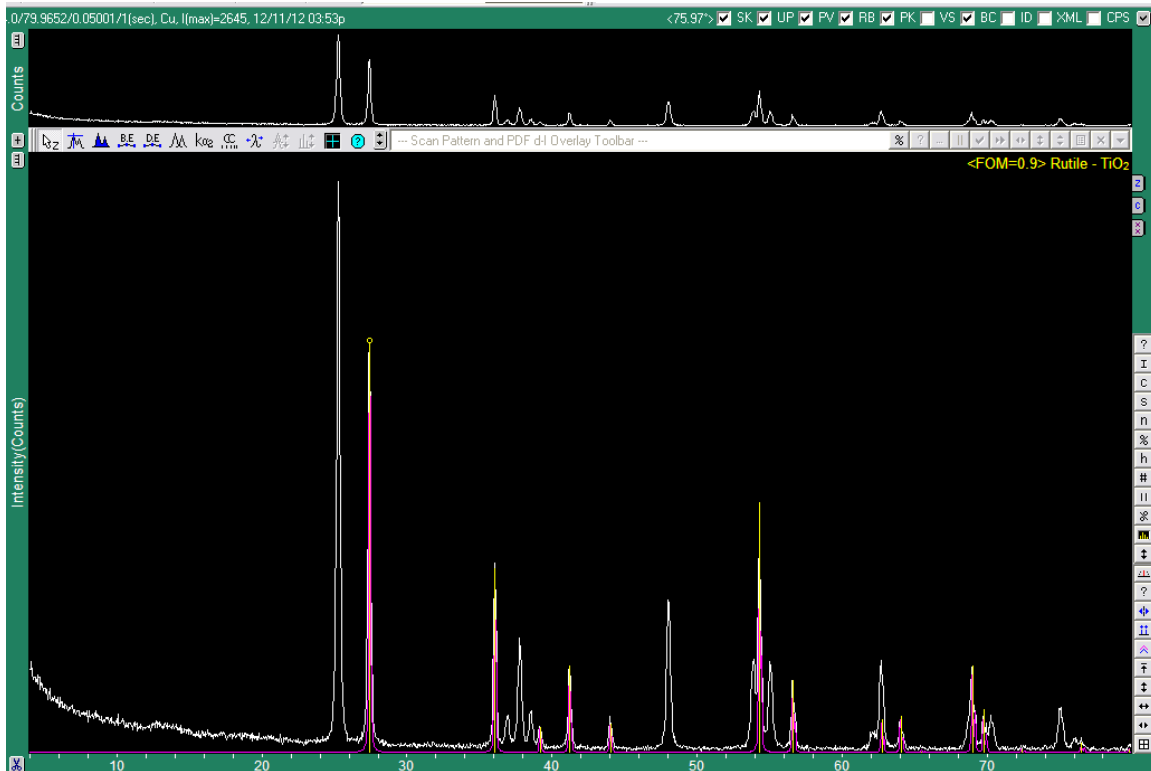


Figure 15 XRD Image of Anatase/Rutile Phase Titania with database Rutile pattern overlay

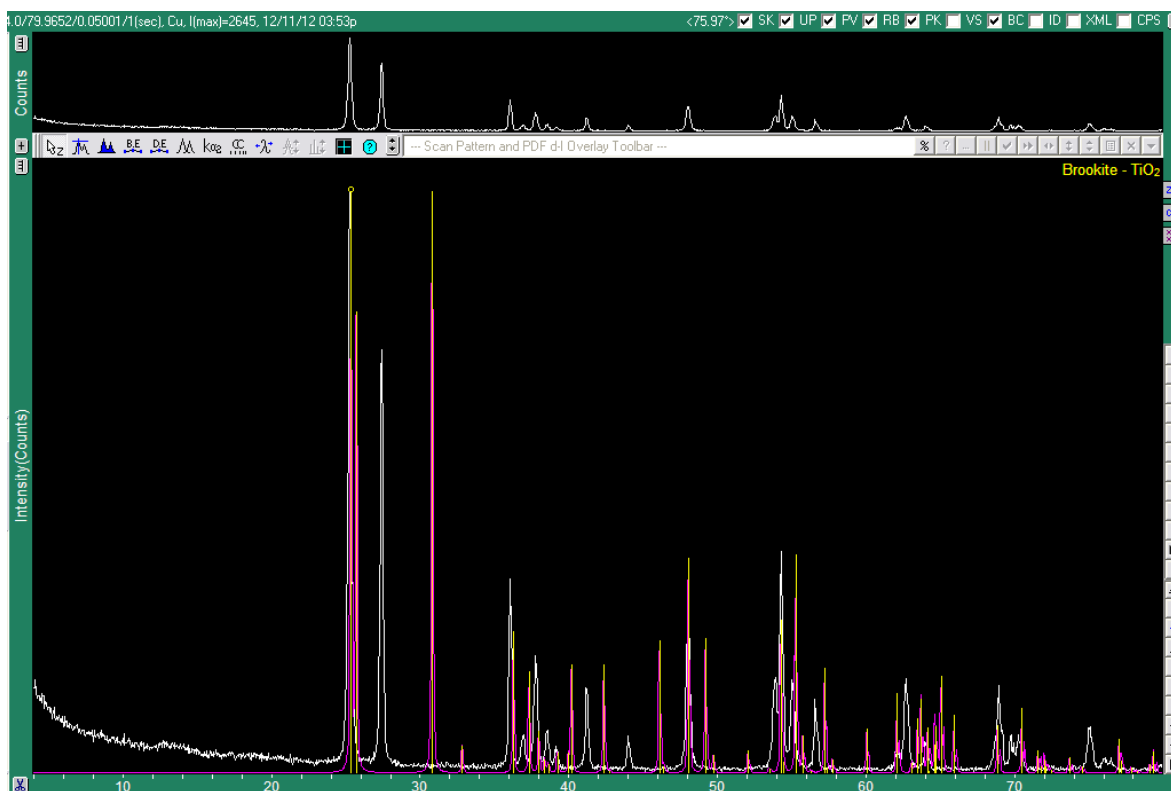


Figure 16 XRD Image of Anatase/Rutile Phase Titania with database Brookite pattern overlay

Of the three patterns, the one that appears to mimic the peaks of the anatase/rutile phase titania samples the best was the anatase pattern. However, there are peaks from the rutile pattern from the database that match adequately with the anatase/rutile phase sample. For example the peaks at 27, 36 and 54 2-theta in the rutile pattern match well with the sample. Yet, there are characteristic peaks seen in the anatase pattern at 25, from 38 to 40 and 48 2-theta that match with the sample. This suggests that the anatase/rutile phase titania sample has structural features that are seen in both anatase and rutile phase titania. The brookite pattern from the database had too many peaks and several that do not match with the sample, such as the one at 31 2-theta that does not appear in the sample pattern. Therefore, it is not likely that the anatase/rutile titania is structurally similar to brookite phase.

4.3 Reactivity Study

A reactivity assessment was performed at pH 7 over the course of 24 hours with each of the photocatalyst phases to determine whether or not CIP reacts without the presence of a UV light source. The results are plotted in the figures below.

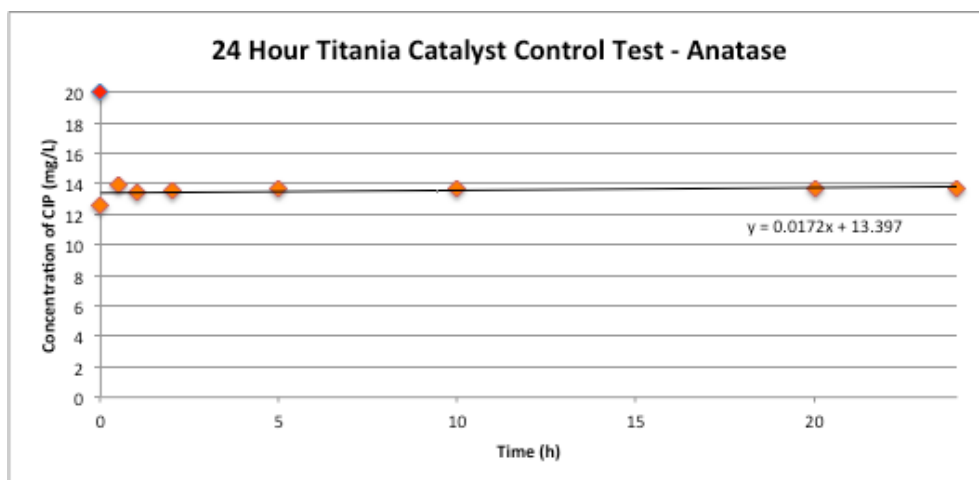


Figure 17 Plot of 24-hour reactivity assessment data for the sample containing anatase titania, no light source.

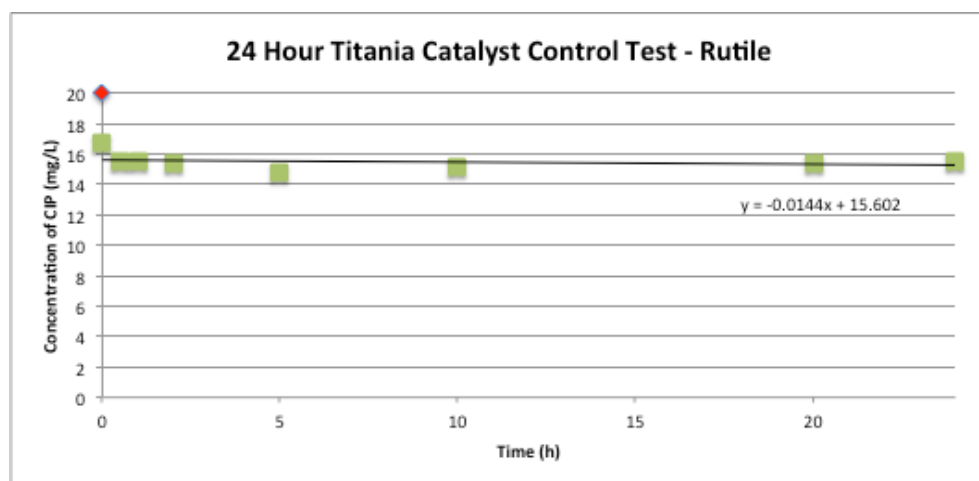


Figure 18 Plot of 24-hour reactivity assessment data for the sample containing rutile titania, no light source.

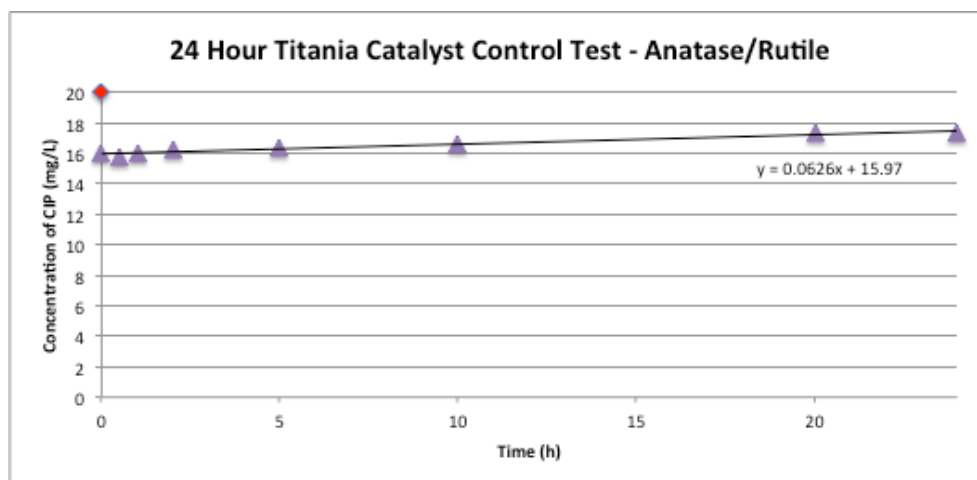


Figure 19 Plot of 24-hour reactivity assessment data for the sample containing anatase/rutile titania

It was determined that CIP in solution with titania does not degrade without the presence of light, as evidenced by the slopes of the trend lines being essentially zero. This was to be expected, since TiO_2 is light activated. In the presence of light, the photons have a higher energy than the semiconductor band gap, resulting in photons being absorbed, and an electron is promoted to the conduction band, leaving a hole in the valence band (Maeda & Domen, 2009). This excited electron is then used directly to drive the chemical reaction.

A peculiar phenomenon was observed when CIP concentrations were measured before adding titania and immediately after adding titania. The solution was measured out to be approximately 20 mg/L of solution (represented by the red diamonds in each graph), However, about thirty seconds after adding the photocatalyst to the solution, there was a drop in CIP concentration, which was neglected when determining the trend lines. It is hypothesized that a small amount of CIP is adsorbed to the surface of the titania particles even before light is applied. This adsorption phenomenon is consistent with the rest of the experiments that involved titania in solution. Additionally, in these figures and even more apparent in the tables in the Appendix, there was an observed slight increase in concentration of CIP throughout the course of 24 hours, which is likely attributed to water evaporation overtime. In summary, it is concluded that in order for a significant degradation of CIP to occur there must be a source of light.

4.4 CIP Degradation

4.4.1 CIP Photocatalytic Degradation with UV

Degradation of CIP in solution was first analyzed using a mercury UV lamp (254 nm). Aside from the control experiment, done without catalyst, each sample contained 1000 mg/L of titania. A

plot of the results obtained for the rate of degradation of CIP using UV photolysis is shown in Figure 20.

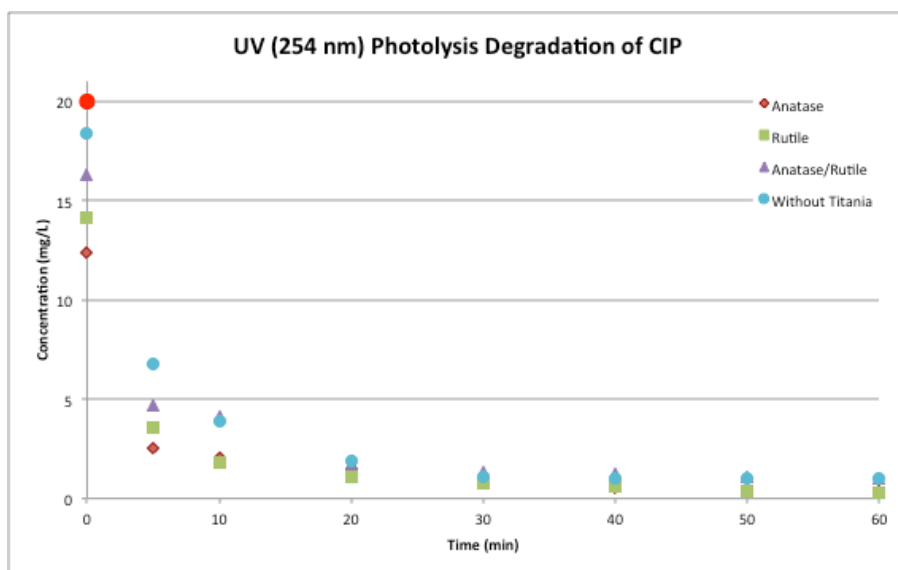


Figure 20 Comparison of titania (1000mg/L) performance under UV photolysis at 254 nm

This plot show that UV photolysis is most effective in the first 20 minutes of light exposure and the final concentration of CIP that remained in solution even after one hour of light exposure was determined to be 0.3 mg/L. Each phase performed comparatively similar, and marginally better than the solution without catalyst in the first ten minutes, yet not much better beyond that when the solutions were exposed to 254 nm of UV light. Again, evidence of adsorption was observed; the red circle represents the measured concentration of ciprofloxacin before adding titania to the samples.

4.4.2 CIP Photocatalytic Degradation with UV-LED

Degradation of CIP in solution was next analyzed using UV light emitting diodes (360 nm). Continuing with the same procedure applied to the first set of photolysis experiments, 1000 mg/L of anatase was added to 20 mg/L CIP solution. Figure 21 displays the results of this experiment.

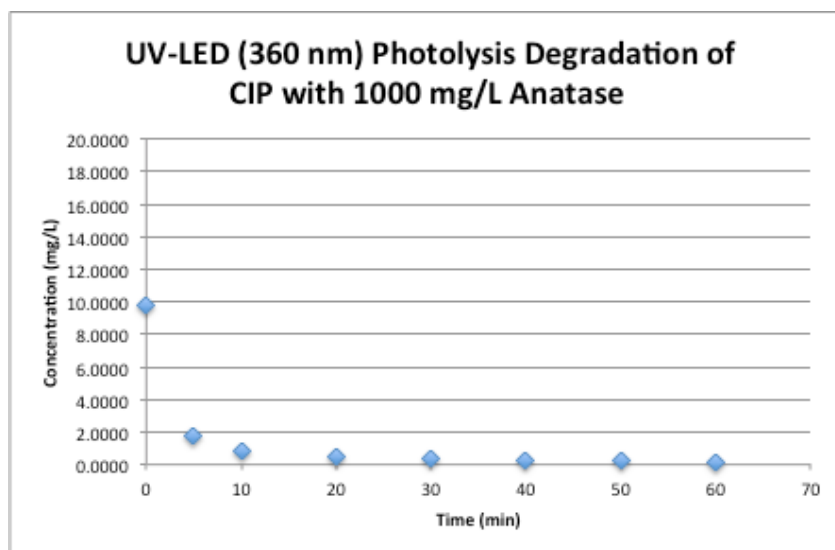


Figure 21 UV-LED photolysis at 360 nm using 1000 mg/L of anatase titania

Since the concentration of CIP dropped to under 2 mg/L after five minutes of light exposure, it was decided to use 500 mg/L of titania in order to more accurately measure the degradation of CIP over time to evaluate the performance of each titania phase under two different light sources. Figure 22 displays the degradation of CIP with 500 mg/L titania exposed to 360 nm UV-LED compared to a control sample without catalyst.

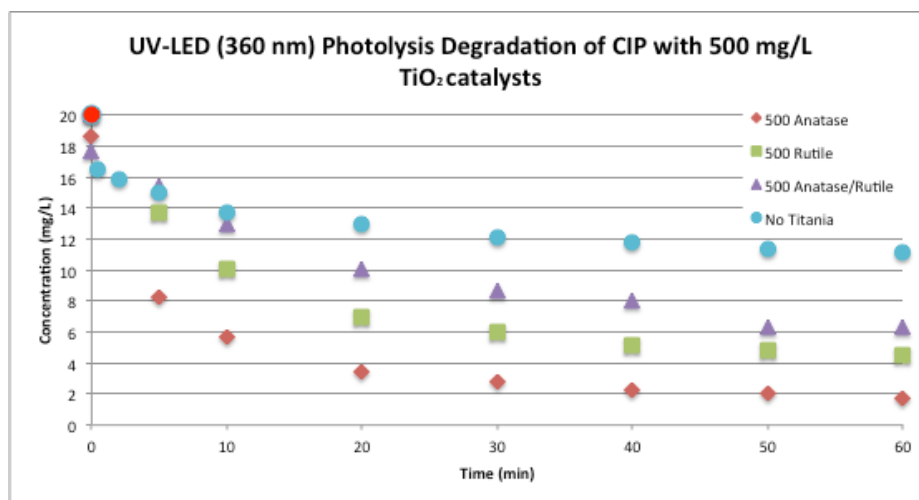


Figure 22 UV-LED photolysis at 360 nm using 500 mg/L of titania

It is apparent that under the 360 nm of UV-LED light, using 14.5 Volts/1 Amp power, anatase exhibited the maximum degradation potential compared to the other phases of titania. This was a unusual result, since it has been found in previous studies that anatase/rutile phases were more photocatalytically active, as stated in the Background. However, it is possible that the

amount of tetrahedral titania at the interface is only a small fraction of the catalyst mass and therefore the tetrahedral orientation would have little effect on the catalyst's photoactivity. Once more, adsorption was apparent when comparing the red data point at $t=0$ to the initial readings after adding the titania to the solution.

It was unexpected to observe that CIP degradation compared between using the mercury UV lamp and the UV light emitting diodes performed better with the mercury lamp. This is apparent in Figure 23.

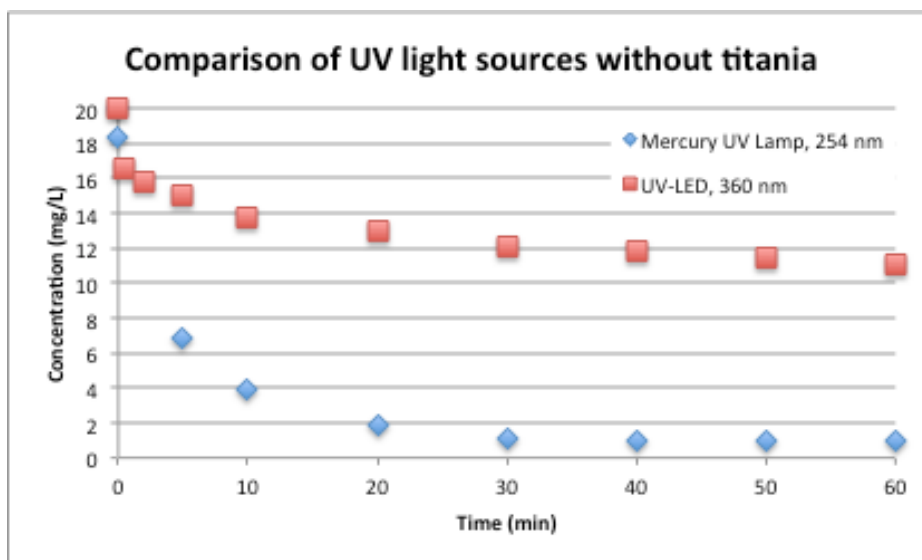


Figure 23 Comparison between the mercury UV lamp (254 nm) and the UV-LEDs (360 nm)

Similarly, a comparison of the results of degradation using 500 mg/L of anatase titania shows that using the mercury UV source produced slightly more efficient degradation, as evident in Figure 24.

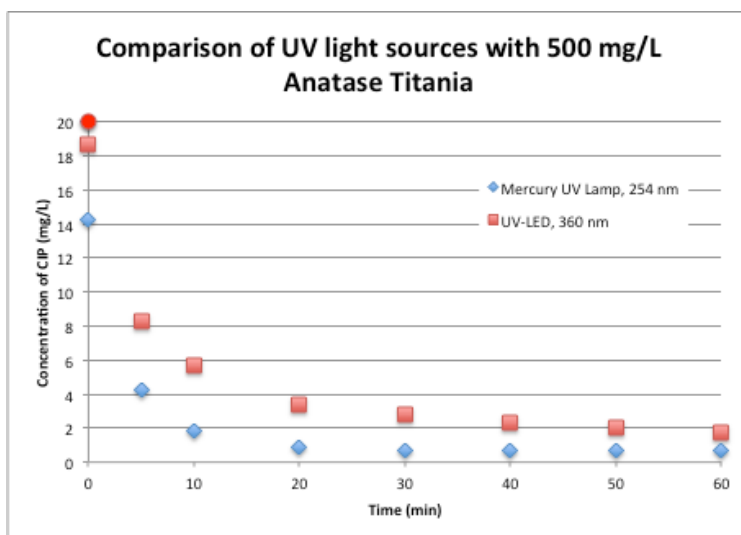


Figure 24 Comparison between the mercury UV lamp (254 nm) and the UV-LEDs (360 nm) using 1000 mg/L of anatase phase titania

While the mercury lamp did appear to outperform the LEDs, it was not by much. After one hour of light exposure, the mercury lamp appeared to degrade less than one mg/L of ciprofloxacin than did the LEDs. For both sources, the most degradation activity occurred in the first twenty minutes of light exposure. After ten minutes, the mercury lamp degraded about 4 mg/L more ciprofloxacin than the LEDs.

However, as stated in the background section, the life expectancy of LEDs is five times that of mercury lamps. Thus, the cost benefit of using the LEDs may outweigh the marginally better performance of the UV mercury lamps. The price of the mercury lamp used in this study was approximately \$250 for the lamp alone. The power supply is priced at approximately \$300. The LEDs are more durable and long lasting, and cost around \$125 for each one. The power supply only cost approximately \$100. Therefore, economically, the LEDs may be the more viable option.

Chapter 5: Conclusions and Recommendations

Both mercury UV lamps (254 nm) and UV light emitting diodes (360 nm) are potentially effective light sources for removing CIP from water under photolysis. However, there does not appear to be any significant difference in the performance between the two light sources under the conditions used in this project. Degradation using the mercury lamp appeared to perform better both without any photocatalyst and with anatase titania. Yet the addition of photocatalyst for the degradation of CIP using the mercury lamp showed to have little effect on the reaction kinetics. Using the LEDs, anatase titania degraded the most CIP. The slight increased activity of the anatase

phase over anatase/rutile was unexpected and should be further investigated. The ciprofloxacin did appear to have an affinity to the surface of all of the photocatalysts. It would be beneficial to explore this adsorptive property of the titanias with other types of pharmaceutical compounds. Additionally, investigating different wavelengths of light would help to determine which conditions provide the best performance of the system.

The LEDs operated with a power supply that provided a maximum voltage of 15-Volts and current of 1.5 amps. In the interests of Aerodyne Research, Inc., the LEDs have a low power requirement; making its use an attractive option for degrading PPCPs. An exploration of several voltages and currents would provide a more definitive conclusion on the effect of power supply has on the reaction. Studying the effect of mixtures of pharmaceuticals in solution could also reveal information about the selectivity of photocatalytic degradation. Aerodyne may also benefit from determining an optimal design for a UV-LED reactor system that maximizes light exposure while continually agitating the solution in the reactor. The reactor system used for this project was unable to ensure that titania was evenly distributed in solution through continuous stirring or agitation. Furthermore, studies using other light sources for comparison in a pilot scale batch reactor would provide additional evidence of UV-LED performance.

While this project did provide data that suggests that the UV-LEDs perform comparatively to the mercury UV lamp, a thorough investigation of the energy considerations and an economic analysis involved with UV-LED photolysis would provide an important supplement to this study. This would allow for a more comprehensive picture of the environmental, energy, and economic advantage of using UV-LEDs as opposed to other light sources.

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Appendix

Appendix A: Standard Curve

Table 1 Data for standard curve

Run	pH	Concentration (mg/L)	Absorbance
1	7.10	21.50	2.0298
2	7.06	10.75	1.1297
3	7.08	5.38	0.4794
4	6.99	2.69	0.2389
5	7.00	1.34	0.1261
6	6.95	0.67	0.0755
7	7.05	0.34	0.0315
8	7.10	0.17	0.0148
9	7.10	0.08	0.0205
10	7.04	0.04	-0.0022

Limit of Detection (LOD) Sample Calculation

Input into Microsoft Excel cell:

$$=STEXY(\text{Absorbance of Run 1: Absorbance of Run 10}, \text{Concentration of Run 1: Concentration of Run 10})$$

$$=0.03757$$

$$LOD = \frac{0.03757}{0.0961} * 3.3 = 1.29 \frac{mg}{L}$$

This is the lowest concentration that the spectrophotometer can distinguish from the blank sample.

Appendix B: Reactivity Assessment

Table 2 24-hour reactivity assessment data, no titania. The first row of data represents the targeted measured concentration of CIP in solution.

Time (h)	Anatase		Rutile		Anatase/Rutile	
	Absorbance	Concentration CIP (mg/L)	Absorbance	Concentration CIP (mg/L)	Absorbance	Concentration CIP (mg/L)
0		20		20		20
0	1.8895	19.66181061	1.6079	16.73152966	1.5362	15.98543184
0.5	1.2132	12.62434964	1.4857	15.45993757	1.5132	15.74609781
1	1.3377	13.91987513	1.4892	15.49635796	1.5376	16
2	1.2858	13.3798127	1.4825	15.42663892	1.5648	16.2830385
5	1.3037	13.566077	1.4175	14.75026015	1.5721	16.35900104
10	1.3105	13.63683663	1.4573	15.16441207	1.5963	16.61082206
20	1.314	13.67325702	1.4793	15.39334027	1.6681	17.35796046
24	1.3179	13.71383975	1.4889	15.49323621	1.6652	17.32778356

Appendix C: UV Photolysis Results

Table 3 UV Photolysis Results, 254 nm mercury UV lamp, 1000 mg/L of catalyst

Time (min)	No Titania		Anatase		Rutile		Anatase/Rutile	
	Absorption	Concentration (mg/L)	Absorbance	Concentration (mg/L)	Absorbance	Concentration (mg/L)	Absorbance	Concentration (mg/L)
0		20		20		20		20
0	1.7641	18.35691988	1.1904	12.38709677	1.3572	14.12278876	1.5632	16.26638918
5	0.6538	6.803329865	0.2464	2.563995838	0.342	3.558792924	0.4542	4.726326743
10	0.371	3.860561915	0.1953	2.032258065	0.1736	1.806451613	0.3959	4.119667014
20	0.1831	1.905306972	0.1427	1.48491155	0.1042	1.084287201	0.164	1.706555671
30	0.1016	1.05723205	0.0899	0.935483871	0.0742	0.772112383	0.1275	1.326742976
40	0.0998	1.038501561	0.0509	0.529656608	0.0559	0.581685744	0.1169	1.216441207
50	0.0962	1.001040583	0.0465	0.483870968	0.0384	0.399583767	0.1032	1.073881374
60	0.0943	0.981269511	0.0323	0.336108221	0.0297	0.30905307	0.0986	1.026014568

Table 4 UV Photolysis Results, 254 nm mercury UV lamp, 500 mg/L anatase catalyst

Time (min)	Anatase 500 mg/L	
	Absorbance	Concentration (mg/L)
0		20
0	1.3653	14.20707596
5	0.4067	4.232049948
10	0.1741	1.811654527
20	0.0833	0.866805411
30	0.0664	0.69094693
40	0.0637	0.662851197
50	0.0623	0.648283039
60	0.0618	0.643080125

Appendix D: UV LED Photolysis Results

Table 5 UV-LED Photolysis Results, 360 nm UV light emitting diodes, 1000 mg/L anatase and 500 mg/L titania

Time (min)	No Titania		1000 Anatase		500 Anatase		500 Anatase/Rutile		500 Rutile	
	Absorption	Concentration (mg/L)	Absorbance	Concentration (mg/L)	Absorbance	Concentration (mg/L)	Absorbance	Concentration (mg/L)	Absorbance	Concentration (mg/L)
0		20		20.0000		20		20		20
0	1.5887	16.5317	0.9400	9.7815	1.7969	18.6982	1.7030	17.7211	1.9836	20.6410
0.5	1.5215	15.8325								
5	1.441	14.9948	0.1674	1.7419	0.7975	8.2986	1.4865	15.4683	1.3170	13.7045
10	1.3178	13.7128	0.0772	0.8033	0.5477	5.6993	1.2421	12.9251	0.9707	10.1009
20	1.2502	13.0094	0.0515	0.5359	0.3282	3.4152	0.9639	10.0302	0.6709	6.9813
30	1.1675	12.1488	0.0390	0.4058	0.2683	2.7919	0.8375	8.7149	0.5824	6.0604
40	1.1362	11.8231	0.0285	0.2966	0.2192	2.2810	0.7708	8.0208	0.4942	5.1426
50	1.0967	11.4121	0.0200	0.2081	0.1971	2.0510	0.6114	6.3621	0.4648	4.8366
60	1.0706	11.1405	0.0167	0.1738	0.1667	1.7347	0.6073	6.3195	0.4306	4.4807